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(54)【発明の名称】　光学的情報記録媒体

(57)【特許請求の範囲】

【請求項１】光、熱等の手段に依ってその光学的性質を可逆的に変化する記録材料層を基板上に備え、その変化を利用して情報の記録、再生、消去を行なう光学的情報記録媒体であって、前記記録材料層が、安定な化学量論的化合物であるGeTeとBi_2Te_3の間の固溶体$xGeTe\ (1-x)\ Bi_2Te_3$（$0<x<1$）であることを特徴とする光学的情報記録媒体。

【請求項２】記録材料層が、安定な化学量論的化合物GeTeとBi_2Te_3の間の固溶体$xGeTe\ (1-x)\ Bi_2Te_3$（$0.1<x<0.85$）であることを特徴とする特許請求の範囲第１項記載の光学的情報記録媒体。

【請求項３】記録材料層の組成が、安定な化学量論的三元化合物$Ge_3Bi_2Te_6$、$GeBi_2Te_4$または$GeBi_4Te_7$もしくは、これらの間の固溶体組成であることを特徴とする特

許請求の範囲第１項記載の光学的情報記録媒体。

【請求項４】記録材料層の組成が、GeTeとBi_2Te_3の間の共晶組成であることを特徴とする特許請求の範囲第１項記載の光学的情報記録媒体。

【発明の詳細な説明】

産業上の利用分野

本発明はレーザー光線等の手段をもちいて情報信号を高速かつ高密度に記録再生し，かつ書き換え可能な光学的情報記録媒体に関するものである。

従来の技術

レーザー光線を金属，色素等の薄膜上に照射して局部的な変化を生じさせ高密度に情報を記録再生する技術は公知であり，追加記録可能なタイプのものが，いわゆるライトワンス（WRITE－ONCE）型光ディスク装置として商品化されている。いっぽう書き換え可能なタイプのも

のは，まだ研究段階であるが，これまで記録層にTe,Se等のカルコゲン，またはその化合物（カルコゲン化物）を主成分とする材料薄膜をもちいるものが提案されてきている。これらの物質，とりわけTeを主成分とする系においては比較的容易にアモルファス相と結晶相との間の可逆的な相変化を生じさせることが可能であり、その間で光学定数が大きく変化することから様々な組成が検討されてきた。

Teは光の赤外領域にも吸収が有ること、融点が400℃程度と低いこと、さらにはその構造の基本が二配位の鎖状の原子結合から成っていることから粘性が大きく、液相から冷却した場合にアモルファス相が形成されやすいこと等、相変化型の書き換え可能な記録材料として望ましい特性を備えている。ただしTe単独では結晶化温度（Tx）が低く室温では安定なアモルファス相をうることができない。そこでTeに様々な添加物元素を加えて、安定なアモルファス相を得る試み、あるいは液晶化の速度をコントロールする試みがなされてきた。

例えば$Ge_1Te_{81}Sb_2S_2$（特公昭47－26897号公報）、$Te_{81}Ge_2As_3$（アプライド　フィジックス　レターズ（APPLIED PHYSICS LETTERS），18（1971）P254），$Te_{87}Ge_8Sn_5$（アプライド　フィジックス　レターズ（APPLIED PHYSICS LETTERS），46（1985）P734）等がある。これはいずれもGe添加によってTeのアモルファス相を安定化している。また結晶化速度を高める試みはTeGeAu系合金（特開昭61－219692号公報），TeGeSnAu系合金（特開昭61－270190号公報）等があり，Auを添加することでTeの鎖状構造を分断し原子の拡散速度を高めることに成功している。

発明が解決しようとする問題点

本発明の目的は、従来の系に比べて、はるかに高速に記録、消去をおこなおうとするものである。

従来、アモルファス－結晶間の相変化を利用する記録－消去方法においては、一般的に結晶相からアモルファス相への変化を記録方向とし逆にアモルファス相から結晶相への変化を消去方向としている。その理由は、結晶化がアモルファス相のアニール、あるいは液相からの徐冷という比較的時間を要するプロセスであるのにたいして、アモルファス化が液相からの急冷という高速のプロセスであるためである。つまり、レーザー光線の照射時間を短くすることができるため記録速度を大きくすることができるということであった。

ところが既に記録ずみの情報信号を消しながら新しい信号を記録してゆく。いわゆる同時消録を行うときには、この結晶化速度もまた十分に大きくする必要がある。つまり結晶化（消去）に要する時間をアモルファス化（記録）に要する時間と同じ程度に短くしなければならない。これまでは、このいわゆる同時消録を実現する手段として記録、再生用と消去用の二つの光スポットを用い、消去用の光スポットの長さを記録、再生用の光スポットの長さよりも相対的に長くすることで消去光スポットの照射時間を長くする方法がとられてきた。しかしながらこの方法は同一トラック上に二つの光スポットを精度よく並べる技術が必要であり、装置の設計上、光学系を複雑にするという問題があった。しかも書き換え速度をこれまでのように高々数百キロバイト/sec程度のスピードからさらに高速化し、例えば磁気ディスクのように数メガバイト/secで記録しようとすると、光スポットと記録媒体との相対速度が数十メートル/secにもなり実際の照射時間は数十nsecと極端に短かくなってしまう。こうなると上述のような光学系で補うといった方法では対応し切れず、真に結晶化速度が大きい材料が必要となる。

問題点を解決するための手段

記録層にTe,Ge,Biの３元系薄膜を採用し、とりわけその組成範囲を全体の組成が化学量論的な化合物組成または、それに準ずる単一相組成となるように選ぶ。

作用

Ge－Bi－Teの三元系においては、GeTeとBi_2Te_3のあいだに$Ge_3Bi_2Te_6$，$GeBi_2Te_4$，$GeBi_4Te_7$といった三元の量論化合物組成が存在する。安定な化学量論的化合物組成においては液体状態（同様にアモルファス状態）と結晶状態との間の自由エネルギーの差が大きく、結晶化のための駆動力を大きくとることができる。また、結晶相が安定な単一相であることから記録、消去の繰り返しによっても相が別れることなく特性が変化するといった問題がない。さらに、この三元系は融点が比較的低くアモルファス相が形成しやすい。結晶化温度が高いことから十分安定なアモルファス相が得られる等、光学記録媒体として優れた特徴を発揮することができる。

実施例

本発明の光学情報記録媒体は、第２図ａ～ｃに示すように、PMMA,ポリカーボネイト等の樹脂、アルミニウム、銅等の金属、ガラス等の表面の平滑な基板１の上にSiO_2、Al_2O_3、ZnS等の誘導体３でサンドイッチした記録層２を形成して構成される。誘導体層は本発明にとっては必ずしも必要ではなく、レーザー光線を繰り返して照射することによる樹脂基材の熱的な損傷、あるいは記録層そのものの変形、蒸発を低減化するために有効である。また、レーザー光の吸収効率を高める目的でレーザー光線の入射する反対側の誘電体層の上に光反射層４をつけること、この上に更に保護板５を張り合わせることも可能である。

本発明は、記録層の組成によって特徴づけられる。記録層はTe,Bi,Geの３元で構成され、その組成の基本は、第１図（ｂ）に示すように二元の化学量論化合物組成GeTeおよびBi_2Te_3をあらわす二つの組成点とを結ぶ線上に位置しており、以下のような組成式で表わすことができる。

$xGeTe\cdot(1-x)Bi_2Te_3$

（$0<x<1$）

以下、本発明の記録媒体において記録層を構成する基本的な考え方、具体的構成元素、ならびに、その濃度を決定する理由について述べる。

上述のようにTe系の記録媒体においてはTeが他の添加物と化合物を形成しうる以上に過剰に含まれる場合、そのことが消去速度を制限する原因となる。そこで添加物の濃度を増やしTeを化学量論組成の化合物として固定する方法が考えられる。しかし、単に一種類の元素を加えただけのTe合金、例えばCdTe,SnTe,PbTe,Sn_2Te_3,Bi_2Te_3,GeTe,$AuTe_2$等は次に述べる理由、

１）融点が高すぎ、レーザー光線の照射時間が短い場合には（記録パルス）容易に溶融することができない。すなわち記録感度が低い。

２）結晶化温度が低すぎて安定なアモルファス相が形成できない。すなわち信頼性に欠ける。

といった、いずれかの、あるいは、両方の理由から記録層としては不適である。

中ではGeTeが安定なアモルファス相と、725℃と比較的低い融点を有しているが、これとても現在の実用的なレーザーダイオードの出力が高々30－40mW程度であることを考えるとアモルファス化が容易ではないうえ、耐湿性が低いという欠点がある。

そこで本発明者等はTeを含む三元系の化合物を検討しGe－Bi－Teの三元化合物が記録薄膜として以下の点で優れていうことを見出した。この系は以下に述べるようにこの系に特異的でかつ重要ないくつかの特性１－４を備えている。

まず第一は、GeTeとBi_2Te_3のあいだには複数の化学量論組成の化合物、すなわち$Ge_3Bi_2Te_6$,$GeBi_2Te_4$,$GeBi_4Te_7$のように両端の二元化合物相の間の三元化合物相が存在することである。第３図にGeTe－Bi_2Te_3擬二元相図を示す。前述のように量論化合物相においては結晶状態における自由エネルギーが低くアモルファス相とのエネルギー準位の差が大きいことから速い結晶化速度が得られる。

第二は上記各化合物相が互いによく似た結晶構造を有し結晶化温度、融点等においても、それぞれ非常に近い値を示すということである。このことは次の効果、即ち、たとえ記録膜組成が厳密に上記化学量論組成相の一つに一致していなくとも、全体としては三つの相間の混合物と見なすことができ、広い組成範囲にわたって特性が変化しないという利点をあたえる。特に、GeTe－Bi_2Te_3の線上では上記、三つの量論化合物組成と全く変わらない特性が得られた。

第三のポイントは上記結晶化温度が十分高く、従って安定なアモルファス相が得られるということである。実施例１中の第４図（ａ），（ｂ），（ｃ）にGeTe－Bi_2Te_3のライン上の組成を含むGe－Bi－Te三元系薄膜の結晶化温度の測定例と、その組成依存性を調べた結果を等高線図として示す。これによって、GeTe－Bi_2Te_3擬二元系

においては、広い領域にわたって室温よりも十分に高い結晶化温度が確保できることがわかる。

第四のポイントは、結晶化課程のなかで見出された。すなわちGeTe－Bi_2Te_3擬二元系においては、その室温における安定な結晶相は六方晶であるが、結晶化の初相として、まずGe,Bi,Teの三元から成る単一な面心立方型の準安定相が現れることが分かった。液体状態あるいはアモルファス状態における原子構造は結晶状態における原子構造よりも遥かに等方的であり、従って生じる結晶形ができるだけ等方的であることが結晶化時における原子の拡散距離を短くし結晶化時間を短縮するうえで有利であると考えられる。面心立方格子は結晶系のなかでも最も等方的なものの一つであることが知られている。準安定相はレーザー照射のように比較的急速に加熱冷却を行う場合に生じやすい。以上の理由によってGe－Bi－Te系薄膜が光学的情報記録媒体として適することがわかる。

次に本発明の製造方法について説明する。本発明の記録媒体は真空蒸着、スパッタリング等の方法で形成することが可能である。スパッタリングについては、望ましい組成から割り出した合金ターゲットを用いることも、各組成に応じた面積の複合モザイクターゲットを用いることも出来る。真空蒸着法の場合は複数のソースを用意し、共蒸着法を採るのが組成のコントロールに便利である。この場合はたとえば三組の電子銃およびその電源、膜厚センサー（例えば水晶振動子）を用意し、各ソースからの蒸着レートを完全に独立して制御できることが望ましい。蒸着時における真空度は、10^{-6}Torrから10^{-7}Torrで十分である。

以下、更に詳しい具体例をもって本発明を詳述する。

実施例１

上記真空蒸着の方法で様々な組成のGe－Bi－Te三元系記録媒体のテストピースを準備し、その特性を調べた。特性の評価は

1.相変態温度Tx

2.アモルファス化に必要な最低レーザー照射パワーP

3.結晶化開始に必要なレーザー照射時間d

の三点から行った。サンプルはTx測定には基板としては厚さ0.3mm、直径8mmのパイレックスガラスを用い、記録層はおよそ100nmの厚さとした。Txはas－depo状態のサンプル片を徐々に加熱していった場合に、その化学的透過率が変化を開始する温度で定義した。昇温は１℃/sのスピードで行い、その間の光学的透過率の変化をHe－Neレーザーを用いてモニターし変曲点を検出した。これによってアモルファス相の熱的安定性が評価できる。

またアモルファス化感度P、結晶化速度dの測定には、基板として縦12mm、横10mm、厚さ1.2mmのPMMA板を用いこの上に100nmのZnS,100nmのGe－Bi－Te三元系記録膜、200nmのZnSを順次蒸着し、その上に基板と同じPMMA板を紫外線硬化樹脂を用いて張り合わせたものを用いた。Pは、ある一定のパルス幅のレーザー光線を結晶状

態の記録膜面に絞りこんで照射し、アモルファス化が開始するのに必要な照射パワーを測定した値をいう。この場合、各サンプルはあらかじめ4mWのパワーで10usの長さのレーザー照射を行って十分に予備黒化（結晶化）をしておき、その後、照射パルス幅を50nsに固定してレーザー出力のみを変化させて照射しアモルファス化が光学的反射率の変化として確認できる照射パワーを測定した。これによって記録感度を評価する。またｄはレーザーダイオードからの光をレンズ系でas－depo状態の記録膜上に直径1um程度のスポットとして照射した場合に結晶化が開始するのに必要な照射時間のことである。この場合、照射パワーを２－25mW、また照射時間を10－1000nsの範囲で変化させて最も速い結晶化の条件を求めた。これによって消去速度の評価をすることができる。

第４図（ａ）はGeTe－Bi_2Te_3系のTxの測定例である。透過率が、ある温度で急激に減少し、結晶化が起こったことがわかる。

（ｂ）は、Ge－Bi－Teの三元組成図上に各組成点に対応するTxをプロットし同一温度の点を結んだ当温線図である。広い組成範囲にわたって室温をはるかに越える転移温度が得られることがわかった。

（ｃ）はGeTeとBi_2Te_3の組成点を結ぶライン上組成に対しGeTeの組成比ｘとTxの関係について調べた結果である。$xGeTe \cdot (1-x)Bi_2Te_3$（０＜ｘ＜１）系の相変態温度は、ｘ＞０のいずれの場合も100℃以上と室温に対して十分に高くアモルファス相が安定に存在することがわかる。更にｘ＞0.1の領域ではTxは140℃以上であり極めて安定なアモルファス状態が得られることがわかった。

第５図は同じ系について結晶化開始に必要なレーザー照射時間を測定した結果である。図中、各カーブは、レーザーパワーを8mWとしたときのGe－Bi－Teの三元組成の結晶化開始パルス幅ｄを各組成点に対応してプロットし同じ温度の点を結んだ等速度線図である。これより、GeTe－Bi_2Te_3のライン上の組成ではおよそ30nsから100nsと極めて短い照射時間で結晶化が開始すること、またラインからはずれるほど結晶化に必要な照射時間が増大することがわかる。ただしライン組成からのずれがそれほど大きくない場合には200ns程度のレーザー照射によって結晶化を開始させることができる。レーザーパワーをさらに高くして同様のことをおこない14mW程度までは結晶化開始のレーザー照射時間の短縮が確認された。

次にアモルファス化感度を調べた。結晶化速度が大きいことは逆にアモルファスが形成されにくい可能性をもっているともいえる。DSCによる融点の測定から上記ライン付近のGe－Bi－Te三元膜の融点は上記ライン上の組成とその周囲とでは比較的近いことがわかったのでGeTe－Bi_2Te_3系を中心にそのアモルファス化感度を調べた。第六図はその結果を示す。これよりGeTeの組成比ｘが0.85よりも小さい領域においては50nsという極めて短い時間のレーザー照射によっても20mW程度のレーザーパワーでアモルファス化が実現していることがわかる。更にGeTeの組成比が33,50,75%という化合物組成ではそれぞれ13,15,17mWというレーザーパワーでアモルファス化が実現している。これらの値はGeTe単体の場合が30mW以上であるのに比較して十分に低くGeTe－Bi_2Te_3系のアモルファス化感度がGeTeに比べて十分に高いことを表わしている。アモルファス化感度は融点と密接に関係しておりBi_2Te_3に近づくほど高くなるがBi_2Te_3単体では先に述べたようにTxがやや低く実用に耐えない。GeTeとBi_2Te_3との間の共晶組成、$Ge_xBi_{2-x}Te_3$においては593℃とこの系の最も低い融点を有することから高い記録感度と比較的安定なアモルファス相を同時に得ることができる。

実施例２

次にGe－Bi－Te三元系薄膜の結晶化課程をＸ線回折およびDSCを用いて調べた結果を示す。厚さ0.3mm,20mm角の石英ガラス上に、ライン上の組成を含む幾つかの組成を約100nm蒸着したテストピースを、それぞれ複数個準備した。各組成において無処理のものおよび、アルゴンガス中で約10分間アニールしたもののＸ線回折パターンを調べた。アニール温度は、あらかじめDSCを用いて結晶化温度等の変態点を調べ、その直上の温度とした。この結果、第一表に示すような結晶化課程が判明した。

第一表　組成と結晶形

組成	無処理	140℃（アニール）	200℃（アニール）
GeBi4Te7	アモルファス	NaCl型	六方晶
GeBi2Te4	アモルファス	NaCl型	六方晶
Ge3Bi2Te6	アモルファス	NaCl型	六方晶
Ge15Bi35Te50	アモルファス	六方晶	六方晶
Ge19Bi25Te56	アモルファス	NaCl型	六方晶
Ge15Bi25Te60	アモルファス	六方晶	六方晶

すなわち、この表から、１）蒸着したままの未処理の状態がアモルファス状態であること、２）上記、ライン上の組成では、まずNaCl型の準安定相が初相として現れていること、３）ラインからはずれた組成では、初めから六方晶の安定相が出現することが読み取れ、ライン上の組成における高速の結晶化が上述の準安定相の出現とよく対応していることがわかる。

DSCからは、ライン上組成に関し、結晶化に伴う発熱ピークも溶融に伴う急熱ピークも共にナローで急峻であることが示され、これらの系が単一相であることが確認された。

実施例３

実施例１、２に対応する各組成点について、光ディスクを試作し、その動特性を調べた。ディスクは、光の案内溝を備えた直径130mm、厚さ1.2mmのPMMA樹脂基板上にZnS,Ge－Bi－Te三元膜、ZnSと順次積層しその上に紫外

線硬化樹脂を用いて基板と同じPMMA板を保護層として張り合わせて構成した。各層の厚さは、下からおよそ800A,1000A,1600Aであり、記録層での光吸収効果を高めるべく設計した。ダイナミックテスター（デッキ）は、記録再生用と消去用とを兼ねた0.9um（1/2強度）径の円形に絞りこんだ一本のレーザースポットを有しており、記録時はレーザー出力を高く消去時は低くすることで古い信号を新しい信号で書きつぶしていく、いわゆるオーバーライト記録をテストするものである。ディスクの回転速度は20m/secを基準とし、5MHzと7MHzの二つの周波数で交互に記録（オーバーライト）をおこなってその繰り返し寿命を調べた。寿命限界としては初期のC/Nから3dB減となる回数と定義し、以下の１）～３）の結論を得た。

１）　ライン上の組成では記録時15－24mW、消去時６－12mWのパワー範囲においてオーバーライトが可能であり、50dB以上のC/Nが得られる。また100万回以上の繰り返しが可能である。また、最大30m/secでのオーバーライト確認された（ランク１）。

２）　ライン上の組成からずれるに従って消去速度の低下から古い信号が消しきれなくなり新しい信号の品質が低下する。この場合は記録周波数を下げ回転速度を10m/sec,5m/secというように遅くすることでライン上の組成の場合と同様にオーバーライトを行える。ただし、あまり大きくはずれてしまうと回転速度では対応できなくなる。また繰り返しによって生じた分相に起因すると思われるノイズが発生しやすくなる。

３）　組成ずれの許容幅は第６図から分かるように上記ラインから見てBiの方向へ＋10at%、Teの方向へ＋10at%程度であって、この範囲では5m/sec以下の回転速度で１万回の繰り返しが可能である（ランク４）。同様にBiの方向に＋7at%,Teの方向に＋5at%程度の範囲では15m/sec以下の回転速度で10万回の繰り返しが可能である（ランク３）。さらに＋5at%，＋3at%程度の範囲では25m/sec以下の回転速度で100万回の繰り返しが可能である（ランク２）。上記各ランクに対応する組成領域を第二表にしめす。

第二表　組成領域と特性

ランク	最大回転速度 m／sec	特性記録／消去パワー (mW／mW)	組成領域 A B C D (Te,Ge,Bi)at%
1.	30	15／6>	ライン上組成 (0.1<X<0.85)
2.	25	15／8>	A(38,59,3) B(50,2,48)
			C(70,2,28) D(63,34,3)
3.	15	12／8>	A(42,55,3) B(53,2,45) C(64.5,2,33.5) D(57,40,3)
4.	5	8／5>	A(44.5,52.5,3) B(55,2,43) C(63,2,35) D(54,43,3)

これらのディスクは、当然のことながら従来のように複数個のレーザースポットを用いても記録／消去をくり返すことが可能であり、むしろそのほうが条件としては選択の自由度が大きく容易であった。

実施例4

実施例１、２におけるディスクの環境試験を行った。各ディスクを80℃,80RH%の環境化に放置し１ケ月の間、反射率をモニターしたが前記Txが140℃以上の組成のディスクについては全く変化が認められなかった。また、錆等の発生も無かった。

発明の効果

本発明によれば、

１）情報の転送レートが毎秒数Mバイトと極めて大きい

２）単一のレーザービームでオーバーライトが可能な

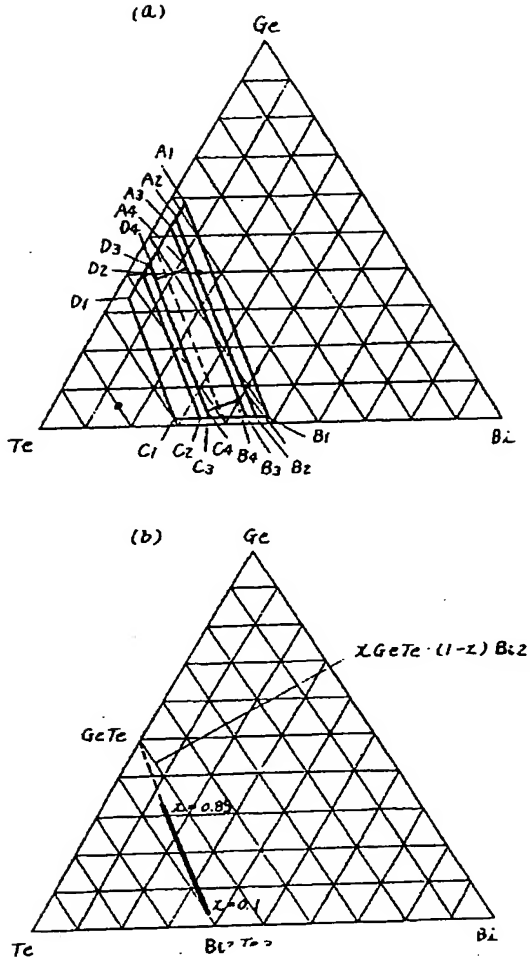
３）繰り返し寿命の長い

光学的情報記録媒体が提供される。

【図面の簡単な説明】

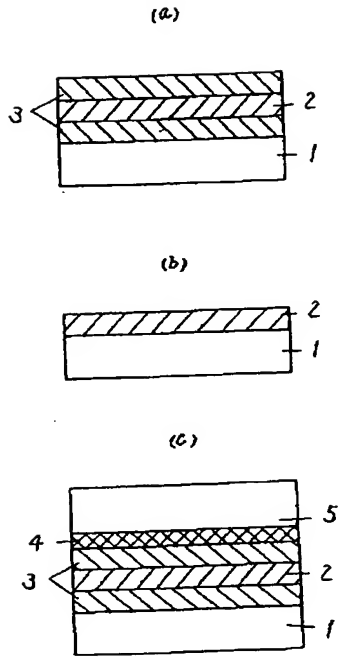
第１図は、本発明の光学情報記録媒体に適用するGe－Bi－Te三元系記録膜の組成領域を示す組成図、第２図は、本発明の一実施例における記録媒体の実施形態例を示す断面図、第３図は、Ge－Bi－Te三元系組成の中心であるGeTe－Bi_2Te_3擬二元系相図、第４図は、結晶化転移温度Txの測定例及び、その組成依存性示す図、第５図は本発明のGe－Bi－Te三元系記録膜のアモルファス化感度の組成依存性示す図、第６図は本発明のGe－Bi－Te三元系記録膜がアモルファス化を開始するのに必要なレーザー照射時間を示す図である。

【第１図】

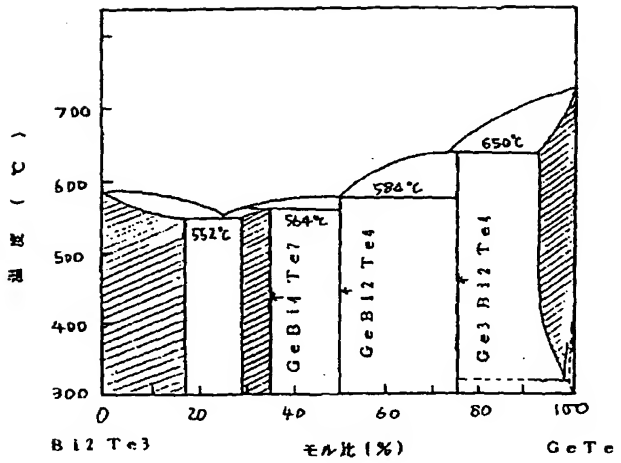


【第２図】

1 … 基板
2 … 記録層
3 … 誘電体
4 … 反射層
5 … 保護板

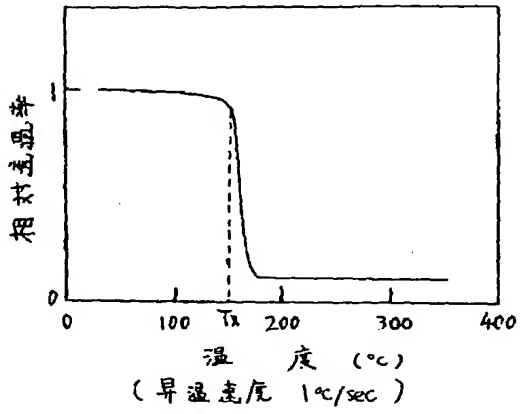


【第3図】



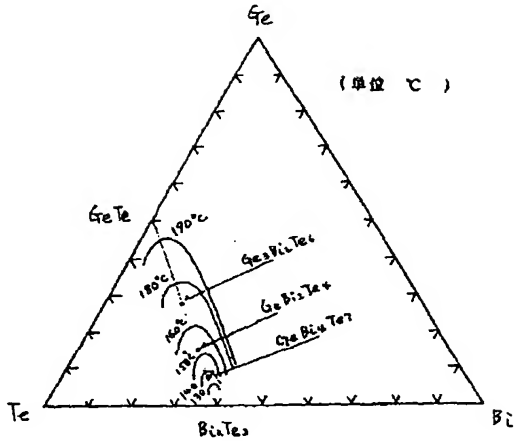
GeTe－Bi2Te3 擬二元系相図

【第4図（a）】



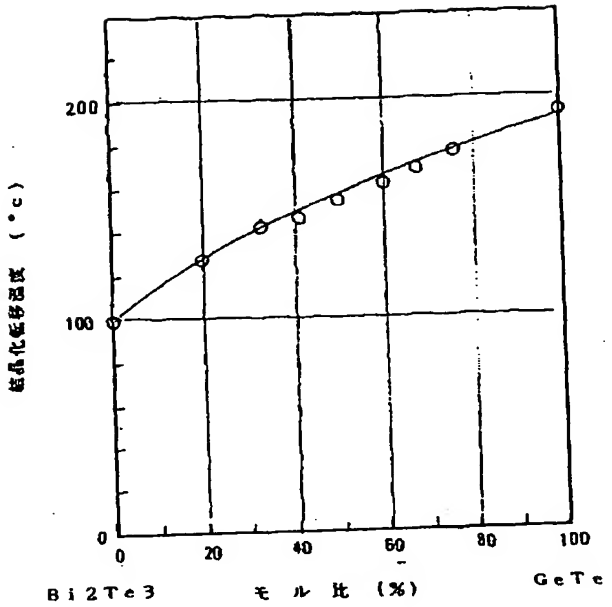
GeBi2Te4の結晶化転移曲線

【第4図（b）】



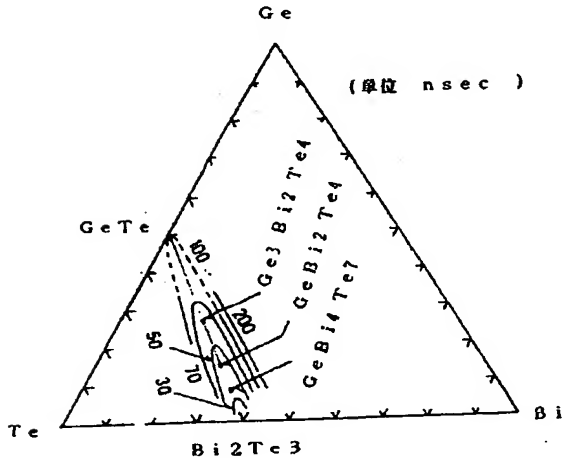
Ge－Bi－Te三元系記録膜の結晶化転移温度と組成

【第4図（c）】



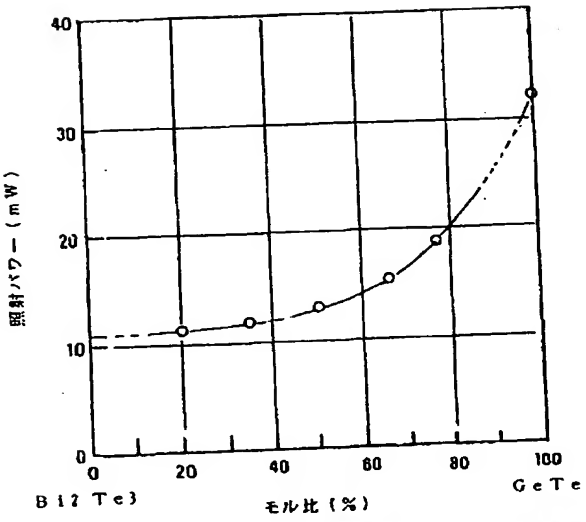
GeTe－Bi2Te3系の結晶化転移温度
（昇温速度　1℃／sec）

【第5図】



Ge－Bi－Te三元系記録膜の結晶化開始に必要な
レーザー照射時間（レーザーパワー　8mW）

【第６図】



ＧｅＴｅ－Ｂｉ２Ｔｅ３系のアモルファス化に必要なレーザーパワー値（照射時間　５０ｎｓｅｃ）

PATENT ABSTRACTS OF JAPAN

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TAKAO MASATOSHI
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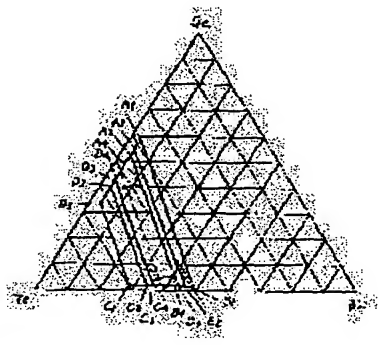
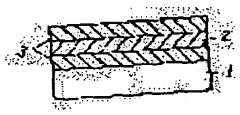
(30)Priority
Priority number : 86 909673 Priority date : 22.09.1986 Priority country : US

(54) OPTICAL INFORMATION RECORDING MEDIUM

(57)Abstract:
PURPOSE: To obtain a medium enabling high density recording, reproduction and rewriting at high speed by using a thin ternary Te-Ge-Bi film as a recording layer and selecting the compsn. rang so as to provide a stoichiometric compd. compsn. or a similar single compsn.
CONSTITUTION: A material represented by a formula xGeTe(1-x) Bi2Te3 is produced from GeTe and Bi2Te3 as solid solns. In case of 0<x<1, the difference in free energy between the liq. phase (amorphous phase) and the crystal phase is large, the phase transition temp. is ≥100° C and the amorphous phase is stably present at room temp. In case of 0.1<x<0.8, a very stable amorphous state is obtd. A recording layer 2 of the material held between SiO2 layers 3 is formed on a substrate 1. When the compsn. of the material is within the region defined with four points A1 (38, 59, 3), B1 (50, 2, 48), C1 (70, 2, 28) and D1 (63, 34, 3); A2 (42, 55, 3), B2 (53, 2, 45), C2 (64.5, 2, 33.5) and D2 (57, 40, 3); A3 (44.5, 52, 3), B3 (55, 2, 43), C3 (63, 2, 35) and D3 (54, 43, 3); or A4 (46.5, 41.5, 12), B4 (54, 6.5, 31.5), C4 (62, 4, 34) and D4 (55, 39, 6) by each compsn. of Te, Ge, Bi a satisfactory recording medium is obtd.





LEGAL STATUS

[Date of request for examination]

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[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

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(57) [Claim(s)]
[Claim 1] The optical information record medium characterized by to be solid-solution xGeTe(1-x) Bi2Te3 (0< x<1) between GeTe which is the optical information record medium which is equipped with the record material layer which therefore changes the optical property to meanses, such as light and heat, in reversible on a substrate, and performs informational record, reproduction, and elimination using the change, and is a stable stoichiometry-[the aforementioned record material layer] compound, and Bi2Te3.
[Claim 2] the claim characterized by a record material layer being stable solid-solution xGeTe(1-x) Bi2Te3 (0.1< x<0.85) between the stoichiometry-compound GeTe and Bi2Te3 -- an optical information record medium given in the 1st term
[Claim 3] The optical information record medium given in the 1st term of a patent claim with which composition of a record material layer is characterized by being stable stoichiometry-ternary-compound germanium3Bi2Te6, GeBi2Te4, GeBi4Te7, or solid-solution composition between these.
[Claim 4] The optical information record medium given in the 1st term of a patent claim with which composition of a record material layer is characterized by being eutectic composition between GeTe and Bi2Te3.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
Field of the Invention this invention is with meanses, such as a laser beam, and relates to the optical information record medium which can carry out record reproduction of the information signal at high speed and with high density, and can be rewritten.
Prior art The technology which irradiates a laser beam on thin films, such as a metal and coloring matter, is made to produce a local change, and carries out record reproduction of the information with high density is well-known, and the type thing in which additional record is possible is commercialized as the so-called write-once (WRITE-ONCE) type optical disk unit. Although the type thing in which ******** rewriting is possible is still a research stage, what is in a record layer until now with the material thin film which makes a principal component chalcogen, such as Te and Se, or the compound (chalcogen ghost) of those has been proposed. It is possible to produce the reversible phase change between an amorphous phase and a crystal phase comparatively easily in these matter and the system which especially makes Te a principal component, and various composition has been considered from an optical constant changing a lot by the meantime.
It has the property desirable as record material which can rewrite a phase-change type -- an amorphous phase is easy to be formed, when that Te has absorption also in the infrared region of light, the melting point's being as low as about 400 degrees C, and viscosity since the foundations of the structure consist of the atomic union of the shape of a chain of 2 coordination further are large and it cools from the liquid phase. However, crystallization temperature (Tx) cannot sell a low amorphous phase stable at a room temperature at a Te independent. Then, various additive elements were added to Te and the attempt which obtains a stable amorphous phase and which tries or controls the speed of liquid-crystal-izing has been made.
For example, there are germanium15Te81Sb2S2 (JP,47-26897,B), Te92germanium2As5 (applied physics Letters (APPLIED PHYSICS LETTERS), 18 (1971)P254), Te87germanium8Sn5 (applied physics Letters (APPLIED PHYSICS LETTERS), 46 (1985)P734), etc. This is all stabilizing the amorphous phase of Te by germanium addition. Moreover, it has succeeded in the attempt which raises crystallization speed having a TeGeAu system alloy (JP,61-219692,A), a TeGeSnAu system alloy (JP,61-270190,A), etc., dividing the chain structure of Te by adding Au, and raising an atomic diffusion rate.
Trouble which invention tends to solve The purpose of this invention tends to perform record and elimination at high speed far compared with the conventional system.
Conventionally, in the record-elimination method of using the phase change during an amorphous-crystal, generally change to an amorphous phase from a crystal phase is made into the record direction, and change to a crystal phase from an amorphous phase is conversely made into the elimination direction. The reason is because amorphous-ization is a high-speed process of quenching from the liquid phase so much, although crystallization is the process of annealing of an amorphous phase, or annealing from the liquid phase which requires time comparatively. That is, since irradiation time of a laser beam was shortened, I hear that recording rate could be enlarged and it was.

However, a new signal is recorded, erasing an information signal [finishing / record / already]. When performing the so-called simultaneous ****, this crystallization speed is also large again enough, and it is necessary to carry out. That is, you have to make it short to the same grade as the time which amorphous-ization (record) takes the time which crystallization (elimination) takes. Until now, the method of lengthening irradiation time of an elimination light spot by lengthening the length of the optical spot for elimination relatively rather than the length of the optical spot for record and reproduction using two optical spots record, the object for reproduction, and for elimination has been taken as a means to realize this so-called simultaneous ****. However, the technology of putting two optical spots in order with a sufficient precision is required for this method on the same truck, and it had the problem of complicating optical system, on the design of equipment. And when it is going to rewrite, and speed tends to be further accelerated like the former from the speed about at most hundreds of K bytes / sec, for example, it is going to record by several megabytes / sec like a magnetic disk, the relative velocity of an optical spot and a record medium is set also to dozens of meters / sec, and actual irradiation time is [dozens of ns and] short ********** extremely. When it becomes like this, by the method of compensating with the above optical system, it does not correspond and go out but material with a very large crystallization speed is needed.

Means for solving a trouble The 3 yuan system thin film of Te, germanium, and Bi is adopted, and it divides to a record layer, and the composition range is chosen so that it may become stoichiometry-[the whole composition] compound composition or a single phase composition according to it.

Operation In the ternary system of germanium-Bi-Te, stoichiometry compound composition of 3 yuan, such as germanium3Bi2Te6, GeBi2Te4, and GeBi4Te7, exists between GeTe and Bi2Te3. In stable stoichiometry-compound composition, the difference of the free energy between a liquid state (it is an amorphous state to this appearance) and a crystallized state is large, and the large driving force for crystallization can be taken. Moreover, there is no problem that a property changes, without a phase separating also by the repeat of record and elimination, since a crystal phase is a stable single phase. Furthermore, the melting point is comparatively low and an amorphous phase tends to form this ternary system. The feature which was excellent as an optical record medium can be demonstrated -- a sufficiently stable amorphous phase is obtained from crystallization temperature being high.

Example As shown in 2nd [**] view a-c, the optical information record medium of this invention forms the record layer 2 sandwiched with the derivatives 3, such as SiO2, aluminum2O3, and ZnS, on the substrate 1 with smooth front faces, such as metals, such as resins, such as PMMA and a polycarbonate, aluminum, and copper, and glass, and is constituted. A derivative layer is not necessarily required for this invention, and it is effective in order to reduction-ize thermal injury on the resin base material by repeating a laser beam and irradiating it or deformation of the record layer itself, and evaporation. Moreover, it is possible to attach the light reflex layer 4 on the dielectric layer of the opposite side in which a laser beam carries out incidence in order to raise the absorption efficiency of a laser beam, and to also make a guard plate 5 rival further on this.

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xGeTe and (1-x) Bi2Te3 ($0< x<1$)

The reason for determining the concentration as the fundamental view which constitutes a record layer in the record medium of this invention, a concrete composition element, and a row hereafter is explained.

More than Te can form other additives and compounds in the record medium of Te system as mentioned above, when it is contained superfluously, it becomes the cause by which that restricts an erasing speed. Then, how to increase the concentration of an additive and fix Te as a compound of a stoichiometric composition can be considered. However, Te alloy which only added one kind of element, for example, CdTe, SnTe, PbTe, Sn2Te3, Bi2Te3, GeTe, and AuTe2 grade are too high, and the reason and the 1 melting point which are described below cannot fuse them easily, when the irradiation time of a laser

beam is short (record pulse). That is, record sensitivity is low.
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In inside, although GeTe has the low melting point comparatively with a stable amorphous phase and 725 degrees C, considering that the output of this and the present practical laser diode is at most about 30 - 40mW, there is a fault of a low in moisture resistance the top for which amorphous-izing is not easy.
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independently. 10-4Torr to 10-7Torr is enough as the degree of vacuum at the time of vacuum evaporationo.
Hereafter, this invention is explained in full detail with a still more detailed example.
Example 1 The test piece of the germanium-Bi-Te ternary system record medium of various composition was prepared by the method of the above-mentioned vacuum deposition, and the property was investigated. Evaluation of a property was performed from three points of the laser radiation time d required for a minimum laser radiation power P3. crystallization start required for the formation of 1. phase-transformation temperature Tx2. amorphous. The sample made the record layer the thickness of about 100nm at Tx measurement, using a Pyrex glass with 0.3mm [in thickness], and a diameter of 8mm as a substrate. When the piece of a sample of an as-depo state was heated gradually, the temperature to which the chemical permeability starts change defined Tx. The temperature up was performed at 1 degree C/s in speed, acted as the monitor of the change of optical permeability in the meantime using helium-Ne laser, and detected point of inflection. This can estimate the thermal stability of an amorphous phase.
Moreover, the vacuum evaporationo of 100nm ZnS, 100nm germanium-Bi-Te ternary system record film, and the 200nm ZnS was carried out one by one on this, using 12mm long, 10mm wide, and a PMMA board with a thickness of 1.2mm as a substrate, and the thing which made the substrate and the same PMMA board rival using ultraviolet-rays hardening resin on it was used for measurement of the amorphous-ized sensitivity P and the crystallization speed d. P narrows down the laser beam of a certain fixed pulse width to the record film surface of a crystallized state, and irradiates it, and the value which measured irradiation power required for amorphous-ization to begin is said. In this case, each sample performs laser radiation of the length of 10us(es) by 4mW power beforehand, fully carries out reserve melanism (crystallization), and measured after that the irradiation power which irradiation pulse width is fixed to 50ns, and only a laser output is changed, irradiates, and amorphous-ization can check as change of an optical reflection factor. This estimates record sensitivity. Moreover, d is irradiation time required for crystallization to begin, when the light from laser diode is irradiated as a spot of about 1 um of diameters on the record film of an as-depo state by the lens system. In this case, irradiation power was changed by two to 25 mW, irradiation time was changed in the range of 10-1000ns, and the conditions of quickest crystallization were searched for. This can estimate an erasing speed.
A view 4 (a) is the example of measurement of Tx of GeTe-Bi2Te3 system. It turns out that permeability decreased rapidly at a certain temperature, and crystallization took place.
(b) is the **** diagram which plotted Tx corresponding to each forming point, and connected the point of the same temperature on the 3 yuan composition diagram of germanium-Bi-Te. It turns out that the transition temperature which exceeds a room temperature far over the large composition range is obtained.
(c) is the result of investigating about the composition ratio x of GeTe, and the relation of Tx to the composition on a line which connects the forming point of GeTe and Bi2Te3. As for the phase-transformation temperature of xGeTe and (1-x) Bi2Te3 ($0< x<1$) system, in any [of $x> 0$] case, it turns out that an amorphous phase exists stably highly enough to 100 degrees C or more and a room temperature. In the field of further $x>0.1$, Tx is 140 degrees C or more, and it turns out that a very stable amorphous state is acquired.
A view 5 is the result of measuring laser radiation time required for a crystallization start about the same system. Each curve is a velocity diagram, such as having plotted crystallization start pulse width d of 3 yuan composition of germanium-Bi-Te when setting a laser power to 8mW corresponding to each forming point, and having connected the point of the same temperature, among drawing. In the composition on the line of GeTe-Bi2Te3, from that crystallization begins by about 30 to 100ns, and very short irradiation time, and a line, this shows that irradiation time required for crystallization increases, so that it shifts. However, when the gap from line composition is not so large, crystallization can be made to start by the laser radiation for about 200ns. The laser power was made still higher, the same thing was performed, and shortening of the laser radiation time of a crystallization start was checked to about 14mW.

Next, amorphous-ized sensitivity was investigated. It can be said that that crystallization speed is large has possibility that amorphous ****** will be hard to be carried out conversely. Since measurement of the melting point by DSC showed that the melting point of the germanium-Bi-Te the film of 3 yuan near [above-mentioned] a line was comparatively near in the composition and the circumference on the above-mentioned line, the amorphous-ized sensitivity was investigated focusing on GeTe-Bi2Te3 system. A view 6 shows the result. It turns out that amorphous-ization is realized by the about 20mW laser power also by the laser radiation of the very short time of 50ns in the field from this where the composition ratio x of GeTe is smaller than 0.85. Furthermore, with 33 and the compound composition of 50 or 75% in the composition ratio of GeTe, amorphous-ization is realized by the laser power of 13 and 15 or 17mW, respectively. These values express that the amorphous-ized sensitivity of GeTe-Bi2Te3 system is fully enough low high compared with GeTe as compared with the case of a GeTe simple substance being 30mW or more. Although it becomes so high that it is closely related to the melting point and Bi2Te3 is approached, as stated previously, with Bi2Te3 simple substance, as for amorphous-ized sensitivity, Tx does not bear practical use a little low. In the eutectic composition between GeTe and Bi2Te3, and germanium4Bi37Te59, high record sensitivity and a comparatively stable amorphous phase can be simultaneously obtained from the thing of 593 degrees C and this system for which it has the low melting point most.

Example 2 The result which used an X diffraction and DSC and next investigated the crystallization course of a germanium-Bi-Te ternary system thin film is shown. Two or more test pieces which deposited about 100nm of some composition including the composition on a line were prepared, respectively on 0.3mm in thickness, and 20mm quartz glass of an angle. Although it annealed for about 10 minutes in a non-processed thing and argon gas in each composition, the X diffraction pattern was investigated. The annealing temperature investigated the transformation points, such as crystallization temperature, using DSC beforehand, and was taken as the temperature of the right above of it. Consequently, the crystallization course as shown in the first table became clear.

第一表　組成と結晶形

組成	無処理	140℃（アニール）	200℃（アニール）
GeBi4Te7	アモルファス	NaCl型	六方晶
GeBi2Te4	アモルファス	NaCl型	六方晶
Ge3Bi2Te6	アモルファス	NaCl型	六方晶
Ge15Bi35Te50	アモルファス	六方晶	六方晶
Ge19Bi25Te56	アモルファス	NaCl型	六方晶
Ge15Bi25Te60	アモルファス	六方晶	六方晶

That is, it turns out that it can read appearing a hexagonal stable phase from the start in the composition shifted from the NaCl type metastable phase having considered as the first phase first from this table by the composition on that a state with unsettled having carried out 1 deposition is in an amorphous state, the 2 above, and a line, and having appeared, and three lines, and corresponds well with the appearance of the metastable phase with high-speed above-mentioned crystallization in the composition on a line. From DSC, about composition on a line, it was shown that both exoergic peaks accompanying crystallization and rapid heating peaks accompanying melting are also steep narrow one, and it was checked that these systems are single phases.

Example 3 About each forming point corresponding to examples 1 and 2, the optical disk was made as an experiment and the dynamic characteristics was investigated. Ultraviolet-rays hardening resin was used for the disk on laminating Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. one by one with ZnS, germanium-Bi-Te the film of 3 yuan, and ZnS on the PMMA resin substrate with an equipped with the guide rail of light diameter [of 130mm], and a thickness of 1.2mm, and it made the same

PMMA board as a substrate rival as a protective layer, and constituted it. The thickness of each class is lower shell about 800A, and 1000A and 1600A, and is the light in a record layer. The dynamic circuit tester (deck) has one laser spot narrowed down circularly [the diameter of 0.9um(s) (1/2 intensity) which served both as the object for record reproduction, and the object for elimination], and the so-called over-writing record which writes and crushes the old signal by the new signal by making a laser output low highly at the time of elimination is tested at the time of record. The rotational speed of a disk recorded by turns on two frequency, 5MHz and 7MHz, on the basis of 20 m/sec (over-writing), and investigated the repeat life. It was defined as the number of times which serves as a 3dB decrease from early C/N as a life limitation, and the following conclusions of 1-3 were obtained.

1) In the composition on a line, and C/N 50dB or more is obtained. [at the time of record] [at the time of 15 to 24 mW and elimination] [in the power range of six to 12 mW] Moreover, 1 million times or more of repeats are possible. moreover, a maximum of 30 m/sec -- the over-writing check was carried out (rank 1)

2) It becomes impossible to be able to finish erasing an old signal from the fall of an erasing speed, and the quality of a new signal deteriorates as it shifts from the composition on a line. In this case, the over-write [lowering record frequency and making rotational speed late like 10 m/sec and 5 m/sec] like the case of composition on a line. When it separates not much greatly, it becomes impossible however, to correspond in rotational speed. Moreover, it becomes easy to generate the noise considered to originate in phase splitting produced by the repeat.

3) The permission width of face of a composition gap concludes that a view 6 shows from the above-mentioned line, is about +10at% in the direction of +10at% and Te to the direction of Bi, and 10,000 times of repeats are possible for it in this range at the rotational speed of 5 or less m/sec (rank 4). In about +5at%, 100,000 times of repeats are possible to the direction of Bi at the rotational speed of 15 or less m/sec in the direction of Te +7at% similarly (rank 3). In about +3at%, 1 million times of repeats are still more possible +5at% at the rotational speed of 25 or less m/sec (rank 2). The composition field corresponding to each above-mentioned rank is shown in the second table.

第二表　組成領域と特性

ランク	最大回転速度 m／sec	特性記録／消去パワー (mW／mW)	組成領域 A B C D (Te,Ge,Bi)at%
1.	30	15／6>	ライン上組成 (0.1<X<0.85)
2.	25	15／8>	A(38,59,3) B(50,2,48)

ランク	最大回転速度 m／sec	特性記録／消去パワー (mW／mW)	組成領域 A B C D (Te,Ge,Bi)at%
			C(70,2,28) D(63,34,3)
3.	15	12／8>	A(42,55,3) B(53,2,45) C(64.5,2,33.5) D(57,40,3)
4.	5	8／5>	A(44.5,52.5,3) B(55,2,43) C(63,2,35) D(54,43,3)

Even if two or more laser spots were used for these disks like before with a natural thing, they can repeat record/elimination, rather, as conditions, the degree of option is large, and it was easier for them.
Example 4 The environmental test of the disk in examples 1 and 2 was performed. Although each disk was left in environment-ization of 80 degrees C and 80RH% and being acted as the monitor of the reflection factor for one month, about the disk of composition of Above Tx of 140 degrees C or more, change was not accepted at all. Moreover, there was also no generating of rust etc.
effect of the invention according to this invention -- 2 with the very large transfer rate of one information as several M bytes/s -- the long optical information record medium of 3 repeat life [over-write / life] is offered by the single laser beam

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[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
Field of the Invention this invention is with meanses, such as a laser beam, and relates to the optical information record medium which can carry out record reproduction of the information signal at high speed and with high density, and can be rewritten.
Prior art The technology which irradiates a laser beam on thin films, such as a metal and coloring matter, is made to produce a local change, and carries out record reproduction of the information with high density is well-known, and the type thing in which additional record is possible is commercialized as the so-called write-once (WRITE-ONCE) type optical disk unit. Although the type thing in which ******** rewriting is possible is still a research stage, what is in a record layer until now with the material thin film which makes a principal component chalcogen, such as Te and Se, or the compound (chalcogen ghost) of those has been proposed. It is possible to produce the reversible phase change between an amorphous phase and a crystal phase comparatively easily in these matter and the system which especially makes Te a principal component, and various composition has been considered from an optical constant changing a lot by the meantime.
It has the property desirable as record material which can rewrite a phase-change type -- an amorphous phase is easy to be formed, when that Te has absorption also in the infrared region of light, the melting point's being as low as about 400 degrees C, and viscosity since the foundations of the structure consist of the atomic union of the shape of a chain of 2 coordination further are large and it cools from the liquid phase. However, crystallization temperature (Tx) cannot sell a low amorphous phase stable at a room temperature at a Te independent. Then, various additive elements were added to Te and the attempt which obtains a stable amorphous phase and which tries or controls the speed of liquid-crystal-izing has been made.
For example, there are germanium15Te81Sb2S2 (JP,47-26897,B), Te92germanium2As5 (applied physics Letters (APPLIED PHYSICS LETTERS), 18 (1971)P254), Te87germanium8Sn5 (applied physics Letters (APPLIED PHYSICS LETTERS), 46 (1985)P734), etc. This is all stabilizing the amorphous phase of Te by germanium addition. Moreover, it has succeeded in the attempt which raises crystallization speed having a TeGeAu system alloy (JP,61-219692,A), a TeGeSnAu system alloy (JP,61-270190,A), etc., dividing the chain structure of Te by adding Au, and raising an atomic diffusion rate.
Trouble which invention tends to solve The purpose of this invention tends to perform record and elimination at high speed far compared with the conventional system.
Conventionally, in the record-elimination method of using the phase change during an amorphous-crystal, generally change to an amorphous phase from a crystal phase is made into the record direction, and change to a crystal phase from an amorphous phase is conversely made into the elimination direction. The reason is because amorphous-ization is a high-speed process of quenching from the liquid phase so much, although crystallization is the process of annealing of an amorphous phase, or annealing from the liquid phase which requires time comparatively. That is, since irradiation time of a laser beam was shortened, I hear that recording rate could be enlarged and it was.

However, a new signal is recorded, erasing an information signal [finishing / record / already]. When performing the so-called simultaneous ****, this crystallization speed is also large again enough, and it is necessary to carry out. That is, you have to make it short to the same grade as the time which amorphous-ization (record) takes the time which crystallization (elimination) takes. Until now, the method of lengthening irradiation time of an elimination light spot by lengthening the length of the optical spot for elimination relatively rather than the length of the optical spot for record and reproduction using two optical spots record, the object for reproduction, and for elimination has been taken as a means to realize this so-called simultaneous ****. However, the technology of putting two optical spots in order with a sufficient precision is required for this method on the same truck, and it had the problem of complicating optical system, on the design of equipment. And when it is going to rewrite, and speed tends to be further accelerated like the former from the speed about at most hundreds of K bytes / sec, for example, it is going to record by several megabytes / sec like a magnetic disk, the relative velocity of an optical spot and a record medium is set also to dozens of meters / sec, and actual irradiation time is [dozens of ns and] short ********** extremely. When it becomes like this, by the method of compensating with the above optical system, it does not correspond and go out but material with a very large crystallization speed is needed.

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Hereafter, this invention is explained in full detail with a still more detailed example.
Example 1 The test piece of the germanium-Bi-Te ternary system record medium of various composition was prepared by the method of the above-mentioned vacuum deposition, and the property was investigated. Evaluation of a property was performed from three points of the laser radiation time d required for a minimum laser radiation power P3. crystallization start required for the formation of 1. phase-transformation temperature Tx2. amorphous. The sample made the record layer the thickness of about 100nm at Tx measurement, using a Pyrex glass with 0.3mm [in thickness], and a diameter of 8mm as a substrate. When the piece of a sample of an as-depo state was heated gradually, the temperature to which the chemical permeability starts change defined Tx. The temperature up was performed at 1 degree C/s in speed, acted as the monitor of the change of optical permeability in the meantime using helium-Ne laser, and detected point of inflection. This can estimate the thermal stability of an amorphous phase.
Moreover, the vacuum evaporationo of 100nm ZnS, 100nm germanium-Bi-Te ternary system record film, and the 200nm ZnS was carried out one by one on this, using 12mm long, 10mm wide, and a PMMA board with a thickness of 1.2mm as a substrate, and the thing which made the substrate and the same PMMA board rival using ultraviolet-rays hardening resin on it was used for measurement of the amorphous-ized sensitivity P and the crystallization speed d. P narrows down the laser beam of a certain fixed pulse width to the record film surface of a crystallized state, and irradiates it, and the value which measured irradiation power required for amorphous-ization to begin is said. In this case, each sample performs laser radiation of the length of 10us(es) by 4mW power beforehand, fully carries out reserve melanism (crystallization), and measured after that the irradiation power which irradiation pulse width is fixed to 50ns, and only a laser output is changed, irradiates, and amorphous-ization can check as change of an optical reflection factor. This estimates record sensitivity. Moreover, d is irradiation time required for crystallization to begin, when the light from laser diode is irradiated as a spot of about 1 um of diameters on the record film of an as-depo state by the lens system. In this case, irradiation power was changed by two to 25 mW, irradiation time was changed in the range of 10-1000ns, and the conditions of quickest crystallization were searched for. This can estimate an erasing speed.
A view 4 (a) is the example of measurement of Tx of GeTe-Bi2Te3 system. It turns out that permeability decreased rapidly at a certain temperature, and crystallization took place.
(b) is the **** diagram which plotted Tx corresponding to each forming point, and connected the point of the same temperature on the 3 yuan composition diagram of germanium-Bi-Te. It turns out that the transition temperature which exceeds a room temperature far over the large composition range is obtained.
(c) is the result of investigating about the composition ratio x of GeTe, and the relation of Tx to the composition on a line which connects the forming point of GeTe and Bi2Te3. As for the phase-transformation temperature of xGeTe and (1-x) Bi2Te3 ($0< x<1$) system, in any [of $x> 0$] case, it turns out that an amorphous phase exists stably highly enough to 100 degrees C or more and a room temperature. In the field of further $x>0.1$, Tx is 140 degrees C or more, and it turns out that a very stable amorphous state is acquired.
A view 5 is the result of measuring laser radiation time required for a crystallization start about the same system. Each curve is a velocity diagram, such as having plotted crystallization start pulse width d of 3 yuan composition of germanium-Bi-Te when setting a laser power to 8mW corresponding to each forming point, and having connected the point of the same temperature, among drawing. In the composition on the line of GeTe-Bi2Te3, from that crystallization begins by about 30 to 100ns, and very short irradiation time, and a line, this shows that irradiation time required for crystallization increases, so that it shifts. However, when the gap from line composition is not so large, crystallization can be made to start by the laser radiation for about 200ns. The laser power was made still higher, the same thing was performed, and shortening of the laser radiation time of a crystallization start was checked to about 14mW.

Next, amorphous-ized sensitivity was investigated. It can be said that that crystallization speed is large has possibility that amorphous ****** will be hard to be carried out conversely. Since measurement of the melting point by DSC showed that the melting point of the germanium-Bi-Te the film of 3 yuan near [above-mentioned] a line was comparatively near in the composition and the circumference on the above-mentioned line, the amorphous-ized sensitivity was investigated focusing on GeTe-Bi2Te3 system. A view 6 shows the result. It turns out that amorphous-ization is realized by the about 20mW laser power also by the laser radiation of the very short time of 50ns in the field from this where the composition ratio x of GeTe is smaller than 0.85. Furthermore, with 33 and the compound composition of 50 or 75% in the composition ratio of GeTe, amorphous-ization is realized by the laser power of 13 and 15 or 17mW, respectively. These values express that the amorphous-ized sensitivity of GeTe-Bi2Te3 system is fully enough low high compared with GeTe as compared with the case of a GeTe simple substance being 30mW or more. Although it becomes so high that it is closely related to the melting point and Bi2Te3 is approached, as stated previously, with Bi2Te3 simple substance, as for amorphous-ized sensitivity, Tx does not bear practical use a little low. In the eutectic composition between GeTe and Bi2Te3, and germanium4Bi37Te59, high record sensitivity and a comparatively stable amorphous phase can be simultaneously obtained from the thing of 593 degrees C and this system for which it has the low melting point most.

Example 2 The result which used an X diffraction and DSC and next investigated the crystallization course of a germanium-Bi-Te ternary system thin film is shown. Two or more test pieces which deposited about 100nm of some composition including the composition on a line were prepared, respectively on 0.3mm in thickness, and 20mm quartz glass of an angle. Although it annealed for about 10 minutes in a non-processed thing and argon gas in each composition, the X diffraction pattern was investigated. The annealing temperature investigated the transformation points, such as crystallization temperature, using DSC beforehand, and was taken as the temperature of the right above of it. Consequently, the crystallization course as shown in the first table became clear.

第一表　組成と結晶形

組成	無処理	140℃（アニール）	200℃（アニール）
GeBi4Te7	アモルファス	NaCl型	六方晶
GeBi2Te4	アモルファス	NaCl型	六方晶
Ge3Bi2Te6	アモルファス	NaCl型	六方晶
Ge15Bi35Te50	アモルファス	六方晶	六方晶
Ge19Bi25Te56	アモルファス	NaCl型	六方晶
Ge15Bi25Te60	アモルファス	六方晶	六方晶

That is, it turns out that it can read appearing a hexagonal stable phase from the start in the composition shifted from the NaCl type metastable phase having considered as the first phase first from this table by the composition on that a state with unsettled having carried out 1 deposition is in an amorphous state, the 2 above, and a line, and having appeared, and three lines, and corresponds well with the appearance of the metastable phase with high-speed above-mentioned crystallization in the composition on a line. From DSC, about composition on a line, it was shown that both exoergic peaks accompanying crystallization and rapid heating peaks accompanying melting are also steep narrow one, and it was checked that these systems are single phases.

Example 3 About each forming point corresponding to examples 1 and 2, the optical disk was made as an experiment and the dynamic characteristics was investigated. Ultraviolet-rays hardening resin was used for the disk on laminating Perilla frutescens (L.) Britton var. crispa (Thunb.) Decne. one by one with ZnS, germanium-Bi-Te the film of 3 yuan, and ZnS on the PMMA resin substrate with an equipped with the guide rail of light diameter [of 130mm], and a thickness of 1.2mm, and it made the same

PMMA board as a substrate rival as a protective layer, and constituted it. The thickness of each class is lower shell about 800A, and 1000A and 1600A, and is the light in a record layer. The dynamic circuit tester (deck) has one laser spot narrowed down circularly [the diameter of 0.9um(s) (1/2 intensity) which served both as the object for record reproduction, and the object for elimination], and the so-called over-writing record which writes and crushes the old signal by the new signal by making a laser output low highly at the time of elimination is tested at the time of record. The rotational speed of a disk recorded by turns on two frequency, 5MHz and 7MHz, on the basis of 20 m/sec (over-writing), and investigated the repeat life. It was defined as the number of times which serves as a 3dB decrease from early C/N as a life limitation, and the following conclusions of 1-3 were obtained.

1) In the composition on a line, and C/N 50dB or more is obtained. [at the time of record] [at the time of 15 to 24 mW and elimination] [in the power range of six to 12 mW] Moreover, 1 million times or more of repeats are possible. moreover, a maximum of 30 m/sec -- the over-writing check was carried out (rank 1)

2) It becomes impossible to be able to finish erasing an old signal from the fall of an erasing speed, and the quality of a new signal deteriorates as it shifts from the composition on a line. In this case, the over-write [lowering record frequency and making rotational speed late like 10 m/sec and 5 m/sec] like the case of composition on a line. When it separates not much greatly, it becomes impossible however, to correspond in rotational speed. Moreover, it becomes easy to generate the noise considered to originate in phase splitting produced by the repeat.

3) The permission width of face of a composition gap concludes that a view 6 shows from the above-mentioned line, is about +10at% in the direction of +10at% and Te to the direction of Bi, and 10,000 times of repeats are possible for it in this range at the rotational speed of 5 or less m/sec (rank 4). In about +5at%, 100,000 times of repeats are possible to the direction of Bi at the rotational speed of 15 or less m/sec in the direction of Te +7at% similarly (rank 3). In about +3at%, 1 million times of repeats are still more possible +5at% at the rotational speed of 25 or less m/sec (rank 2). The composition field corresponding to each above-mentioned rank is shown in the second table.

第二表　組成領域と特性

ランク	最大回転速度 m／sec	特性記録／消去パワー (mW／mW)	組成領域 A B C D (Te,Ge,Bi)at%
1.	30	15／6>	ライン上組成 (0.1<X<0.85)
2.	25	15／8>	A(38,59,3) B(50,2,48)

ランク	最大回転速度 m／sec	特性記録／消去パワー (mW／mW)	組成領域 A B C D (Te,Ge,Bi)at%
			C(70,2,28) D(63,34,3)
3.	15	12／8>	A(42,55,3) B(53,2,45) C(64.5,2,33.5) D(57,40,3)
4.	5	8／5>	A(44.5,52.5,3) B(55,2,43) C(63,2,35) D(54,43,3)

Even if two or more laser spots were used for these disks like before with a natural thing, they can repeat record/elimination, rather, as conditions, the degree of option is large, and it was easier for them.
Example 4 The environmental test of the disk in examples 1 and 2 was performed. Although each disk was left in environment-ization of 80 degrees C and 80RH% and being acted as the monitor of the reflection factor for one month, about the disk of composition of Above Tx of 140 degrees C or more, change was not accepted at all. Moreover, there was also no generating of rust etc.
effect of the invention according to this invention -- 2 with the very large transfer rate of one information as several M bytes/s -- the long optical information record medium of 3 repeat life [over-write / life] is offered by the single laser beam

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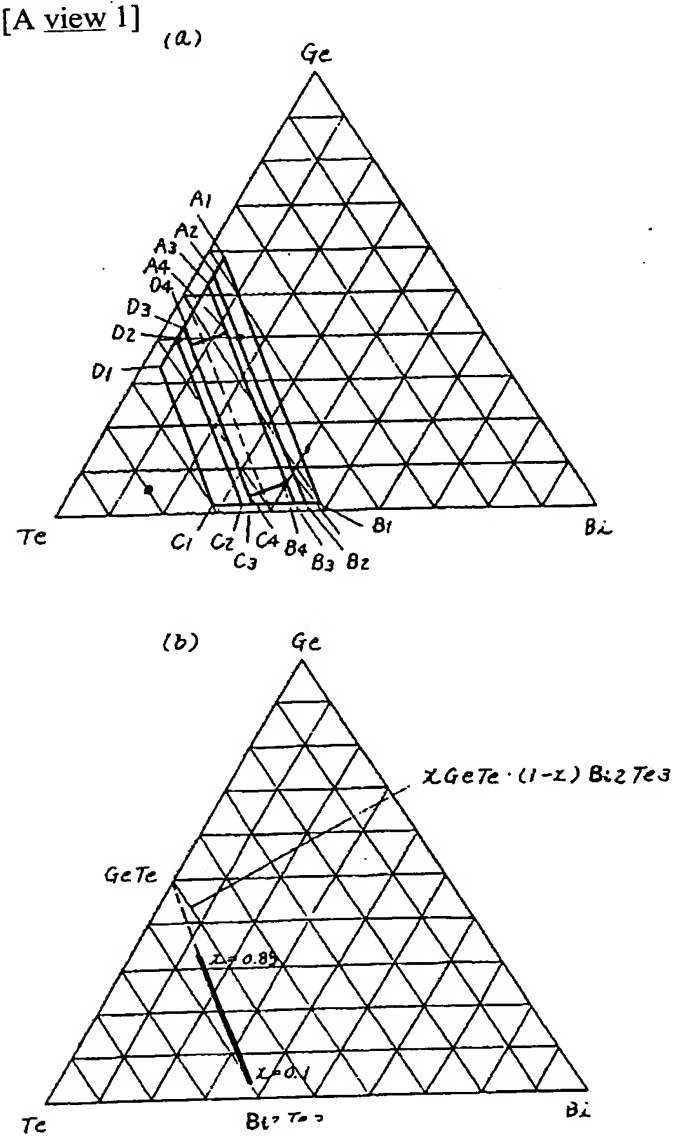
[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

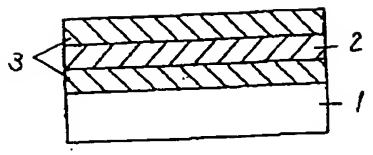
[A view 1]



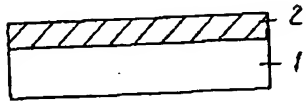
[A view 2]

1 … 基板
2 … 記録層
3 … 誘電体
4 … 反射層
5 … 保護板

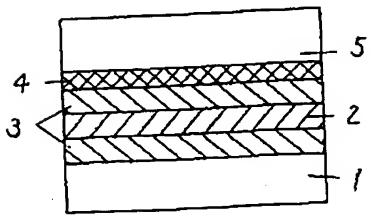
(a)



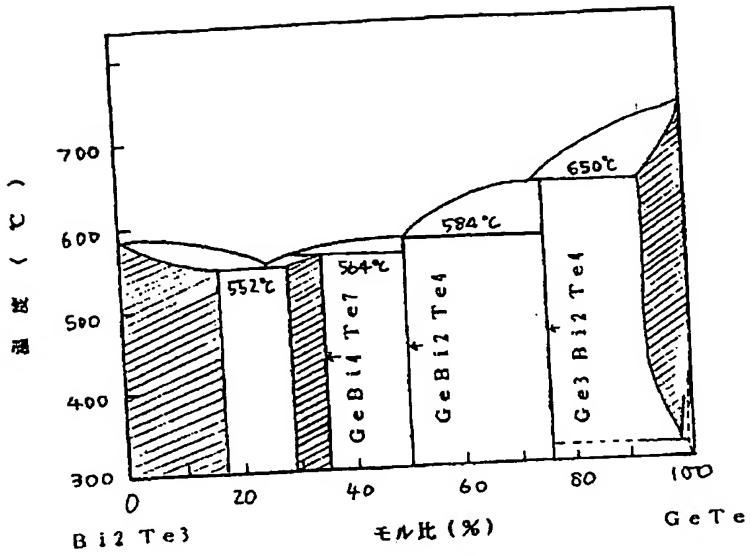
(b)



(c)

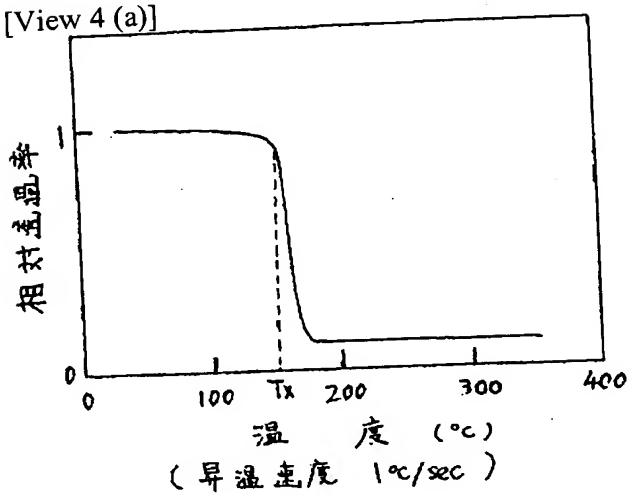


[A view 3]



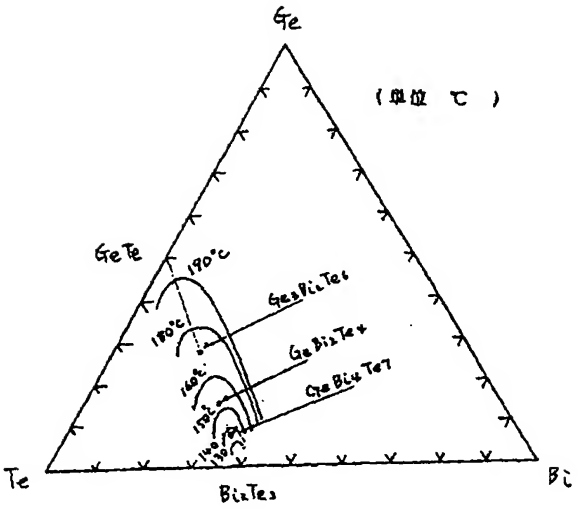
GeTe－Bi2Te3 擬二元系相図

[View 4 (a)]



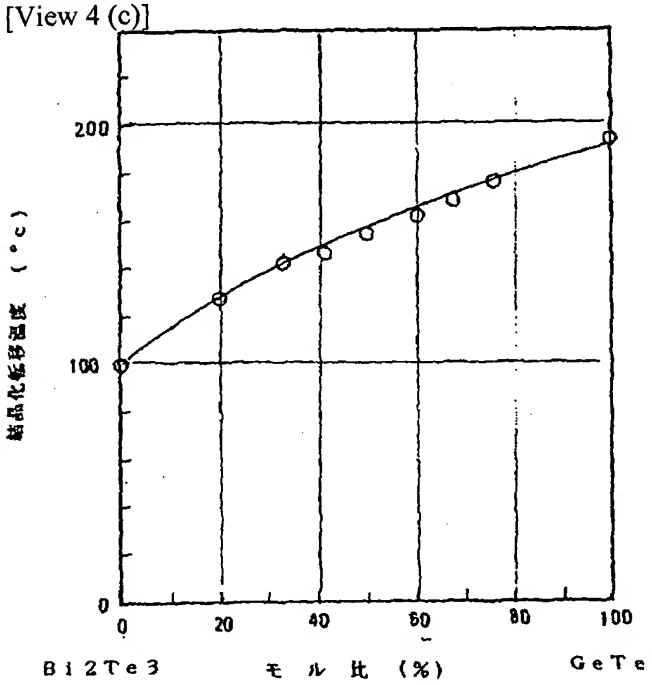
GeBi2Te4の結晶化転移曲線

[View 4 (b)]



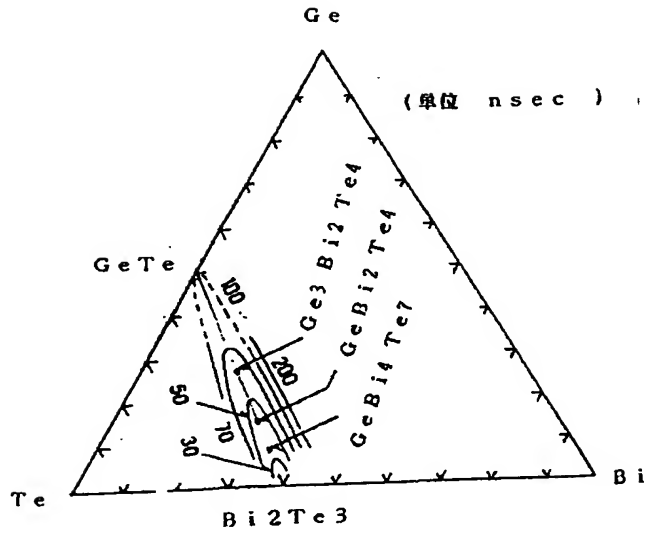
Ｇｅ－Ｂｉ－Ｔｅ三元系記録膜の結晶化転移温度と組成

[View 4 (c)]



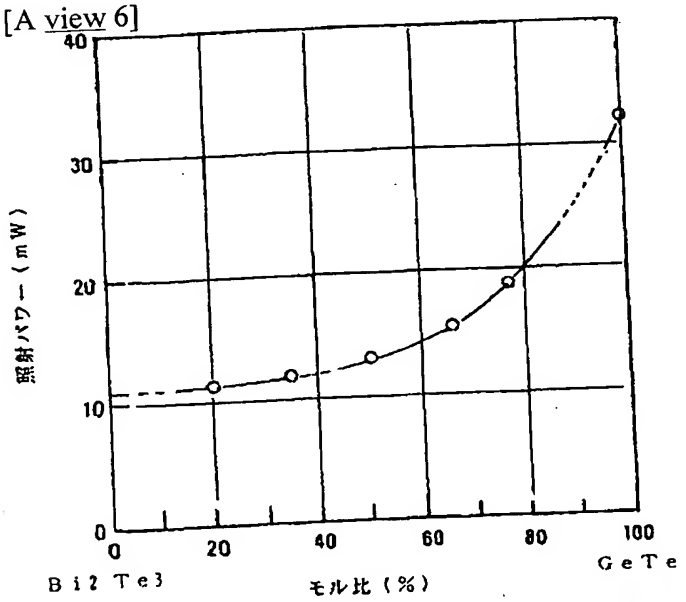
ＧｅＴｅ－Ｂｉ２Ｔｅ３系の結晶化転移温度
(昇温速度 1℃／ｓｅｃ)

[A view 5]



Ge－Bi－Te三元系記録膜の結晶化開始に必要な
レーザー照射時間（レーザーパワー 8mW）

[A view 6]



GeTe－Bi2Te3系のアモルファス化に必要な
レーザーパワー値 （照射時間 50nsec）

[Translation done.]